recrystallized from petroleum ether (65–110°). The yield was 68%, m.p. 149–159°.

Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 78.00; H, 7.79; N, 4.33. Found: C, 78.09; H, 7.64; N, 4.26.

1-(2-Hydroxyethyl)-2,6-diphenyl-3,3-dimethyl-4-piperidone (XXXIII). A mixture of 14 g. (0.05 mole) of 2,6-diphenyl-3,3-dimethyl-4-piperidone, 3.52 g. (0.08 mole) of ethylene oxide, and 20 ml. of methanol was heated at 95–100° under pressure for 24 hr. After removing the solvent *in vacuo*, the viscous residue was covered with petroleum ether and allowed to stand in a refrigerator until the material crystallized. It was recrystallized from petroleum ether. The yield was 81%, m.p. 104–104.5°.

Anal. Calcd. for $C_{21}H_{25}NO_2$: C, 78.00; H, 7.79; N, 4.33. Found: C, 77.90; H, 7.59; N, 4.30.

1-(2-Hydroxyethyl)-2,6-diphenyl-3,5-dimethyl-4-piperidinol (XXXIV). Compound XXXII was hydrogenated in glacial acetic acid with platinum as a catalyst. The acetic acid was removed *in vacuo* and the residue was recrystallized from benzene. The yield was 74%, m.p. 186–186.5°.

Anal. Calcd. for $C_{21}H_{27}NO_2$: C, 77.51; H, 8.37; N, 4.31. Found: C, 77.39; H, 8.34; N, 4.27.

1-(2-Hydroxyethyl)-1-methyl-2,6-diphenyl-3,5-dimethyl-4-ketopiperridinium iodide (XXXV). A mixture of 0.5 g. (0.0015 mole) of 1-(2-hydroxyethyl)-2,6-diphenyl-3,5-dimethyl-4-piperidone and 3 g. (0.021 mole) of methyl iodide was heated at 100° under pressure for 68 hr. Excess methyl iodide was removed *in vacuo* and the residue was recrystallized from 95% ethyl alcohol. The yield was 46%, m.p. 203.5–204.5°.

Anal. Calcd. for $C_{22}H_{28}NO_2I$: C, 56.76; H, 6.06; N, 3.01; I, 27.26. Found: C, 56.90; H, 6.15; N, 3.02; I, 27.19.

1-(2-Hydroxyethyl)-1-methyl-2,6-diphenyl-3,3-dimethyl-4-ketopiperridinium iodide (XXXVI). A mixture of 9.6 g. (0.03 mole) of 1-(2-hydroxyethyl)-2,6-diphenyl-3,3-dimethyl-4-piperidone and 21.1 g. (0.15 mole) of methyl iodide was heated at 100° under pressure for 72 hr. Excess methyl iodide was removed *in vacuo* and the residue was recrystallized from ethanol-ether. The yield was 30%, m.p. 209.5–210.5°.

Anal. Calcd. for $C_{22}H_{28}NO_2I$: C, 56.76; H, 6.06; N, 3.01; I, 27.26. Found: C, 57.00; H, 6.07; N, 3.07; I, 27.06.

1-(2-Hydroxyethyl)-1-methyl-2,6-diphenyl-3,5-dimethyl-4-hydroxypiperidinium iodide (XXXVII). A mixture of 8.1 g. (0.025 mole) of 1-(2-hydroxyethyl)-2,6-diphenyl-3,5-dimethyl-4-piperidinol and 21.1 g. (0.15 mole) of methyl iodide was heated at 100° under pressure for 96 hr. Excess methyl iodide was removed *in vacuo* and the residue was recrystallized from dry ethanol. The yield was 53%, m.p. 219–220°.

Anal. Calcd. for $C_{22}H_{30}NO_2I$: C, 56.54; H, 6.47; N, 3.00; I, 27.15. Found: C, 56.43; H, 6.40; N, 2.88; I, 27.32.

Preparation of p-nitro and p-aminobenzoates of XIX *and* XX. These derivatives were prepared by the usual procedures, namely *p*-nitrobenzoylation in pyridine solution and subsequent reduction of the nitro group with hydrogen and palladium.

p-Nitrobenzoate of 2,2,6,6-tetramethyl-4-piperidinol (XXXVIII). The product was recrystallized from 95% ethyl alcohol; yield 49%, m.p. 128.5–129.5°.

Anal. Calcd. for $C_{16}H_{22}N_2O_4$: C, 62.71; H, 7.24; N, 9.15. Found: C, 62.71; H, 7.12; N, 9.18.

p-Aminobenzoate of 2,2,6,6-tetramethyl-4-piperidinol (XXXIX). The product was recrystallized from water; yield 95%, m.p. 146–147°.

Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.14. Found: C, 69.30; H, 8.86; N, 9.96.

p-Nitrobenzoate of 2,2,6-trimethyl-4-piperidinol (XL). This compound was recrystallized from 95% ethyl alcohol; yield 48%, m.p. 93–94°.

Anal. Calcd. for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.89; N, 9.58. Found: C, 61.50; H, 6.95; N, 9.47.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Some Derivatives of ϵ-Caprolactam[1,2]

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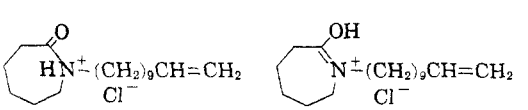
A method for the *N*-alkylation of ϵ-caprolactam has been developed and used to produce the *N*-*n*-butyl, *N*-*n*-hexyl and the *N*-undecenyl derivatives. All of these amides showed markedly basic properties. Hydrolysis of *N*-undecenyl-ϵ-caprolactam with hydrochloric acid solution led to the formation of *N*-10(11?)-chloroundecyl-ϵ-aminocaproic acid which was characterized as the *N*-*p*-toluenesulfonyl derivative. *N*-*p*-Toluenesulfonyl-ϵ-aminocaproic acid was prepared and found to undergo cyclization forming *N*-*p*-toluenesulfonyl-ϵ-caprolactam when treated with either phosphorus pentachloride or sulfuric acid. The benzyl esters of *N*-benzoyl-ϵ-aminocaproic acid and *N*-formyl-ϵ-aminocaproic acid were synthesized.

In connection with the synthesis of a polyampholyte of regular structure, work was directed toward the preparation of a suitable intermediate from ϵ-caprolactam. Although this route to a polyampholyte proved to be infeasible, a number of previously unreported derivatives of ϵ-caprolactam were made.

A general procedure for the *N*-alkylation of ϵ-caprolactam was developed and the properties of the *N*-alkyl-ϵ-caprolactams were briefly investigated. All were found to have a pronounced basic character, forming perbromide and hygroscopic hydrogen chloride salts readily. In the case of *N*-undecenylcaprolactam a crystalline hydrochloride was isolated and the infrared absorption of this compound indicated it to be a mixture of the two isomers shown below. While ϵ-caprolactam itself and *N*-methyl-ϵ-caprolactam are easily hydrolyzed,



(1) Abstracted from a portion of the Ph.D. thesis of Wendell W. Moyer, Jr., University of Illinois, 1957.

(2) The work discussed herein was performed as a part of the synthetic rubber research project sponsored by the National Science Foundation.

the higher *N*-alkyl derivatives may be hydrolyzed only with difficulty.

A somewhat surprising cyclization was found to occur when *N*-*p*-toluenesulfonyl-ε-aminocaproic acid was treated with either catalytic amounts of sulfuric acid under esterification conditions or with phosphorus pentachloride in benzene. *N*-*p*-Toluenesulfonyl-ε-caprolactam was recovered in both cases as the primary reaction product.

EXPERIMENTAL[3]

N-n-Butyl-ε-caprolactam. 1. *Sodium hydride alkylation method of Fones.*[4] Into a 500-ml. three-necked flask, fitted with a stirrer, reflux condenser with calcium chloride drying tube, and dropping funnel, were placed 2.40 g. (0.10 mole) of sodium hydride and 11.32 g. (0.10 mole) of ε-caprolactam in 200 ml. of dry xylene. The stirrer was started and the mixture was heated under reflux in an atmosphere of nitrogen for 10 hr. After cooling somewhat, a mixture of 27.4 g. (0.2 mole) of *n*-butyl bromide and 50 ml. of dry xylene was added and the reaction mixture was heated under reflux with stirring for 4 hr. The hot mixture was filtered, the residual sodium bromide was washed with 50 ml. of dry benzene, and the filtrate and washings were combined. Distillation of the solvent under diminished pressure followed by fractionation of the residual liquid yielded 11.85 g. (70%); b.p. 137–140° (17 mm.); n_D^{20} 1.4782.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.98; H, 11.32. Found: C, 70.24; H, 11.06.

The infrared spectrum contains a significant band at 1645 cm.$^{-1}$ indicating the presence of a disubstituted amide and is consistent with the expected structure. A hydrochloride derivative was prepared but was not characterized because of its hygroscopic nature.

2. *Sodium method.* Into a 500-ml. three-necked flask fitted with a stirrer, reflux condenser with a calcium chloride drying tube, and dropping funnel, were placed 200 ml. of dry xylene, 2.30 g. (0.10 g.-atom) of powdered sodium and 11.32 g. (0.10 mole) of ε-caprolactam. The mixture was heated under reflux with stirring for 4 hr. After cooling slightly, 20.6 g. (0.15 mole) of *n*-butyl bromide was added dropwise to the reaction mixture. The mixture was then heated under reflux with stirring for 8 hr., cooled to room temperature, and filtered in order to remove the precipitated sodium bromide. The precipitate was washed several times with dry benzene and the combined filtrate and washings were evaporated. Distillation of the residual liquid through a 10-inch Vigreux column yielded 13.23 g. (78.1%); b.p. 130–137° (15 mm.).

N-n-Hexyl-ε-caprolactam. The sodium hydride procedure was carried out using 19.8 g. (0.12 mole) of *n*-hexyl bromide in place of the *n*-butyl bromide. Distillation of the residual liquid yielded 14.9 g. (75% of theory); b.p. 190–197° (30 mm.); 167–174° (20 mm.) n_D^{20} 1.4754.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.04; H, 11.75. Found: C, 73.29; H, 11.50.

The infrared spectrum of this compound is almost identical with that of N-*n*-butyl-ε-caprolactam and is in agreement with the expected structure. Impure hydrochloride and perbromide salts were prepared but were not characterized.

N-Undecenyl-ε-caprolactam. This compound was prepared by the sodium alkylation procedure used for the preparation of the *N*-butyl derivative. The only modifications were the use of an equivalent amount, 23.3 g. (0.10 mole), of undecylenyl bromide, and an allowance for longer heating under reflux. The crude product was purified by distillation under reduced pressure yielding 16.65 g. (63%); b.p. 160–165° (0.8 mm.); 165–168° (1 mm.); n_D^{20} 1.4797.

Anal. Calcd. for $C_{17}H_{31}NO$: C, 76.92; H, 11.77. Found: C, 76.65; H, 11.51.

The infrared spectrum contains bands assignable to a disubstituted amide (1645–50 cm.$^{-1}$) and to a terminal vinyl group (978, 910 cm.$^{-1}$).

The hydrogen chloride salt was prepared by bubbling dry hydrogen chloride gas into an ethereal solution of the *N*-alkyl derivative. The derivative had a melting point of 74.5–77.5°. The infrared spectrum of a Nujol mull gave principal bands at 3080, 2905, 2840, 2530, 2065, 1965–80, 1765, 1632, 1477, 1435, 1390, 1325, 991 and 912 cm.$^{-1}$ indicating a mixture of the two salts mentioned before. The product loses hydrogen chloride on drying in a vacuum and a good analysis was not obtained on the product. A 10,11-dibromoundecenyl-ε-caprolactam perbromide salt was prepared by adding bromine to an ice-cold ethereal solution of the *N*-undecenyl compound. The perbromide salt precipitated from the ethereal solution as an orangish red viscous oil. The infrared spectrum contains a band assignable to a disubstituted amide salt (1732 cm.$^{-1}$).

N-p-Toluenesulfonyl-N-10(or 11?)-chloroundecyl-ε-aminocaproic acid. In a 500-ml. flask fitted with a reflux condenser were placed 15.0 g. (0.057 mole) of *N*-undecenyl-ε-caprolactam and 200 ml. of 18% hydrochloric acid. After heating under reflux continuously for seven days, the hot solution was transferred to a 500-ml. beaker and allowed to cool to room temperature. An oily layer separated and solidified on standing. This product was presumably the hydrogen chloride salt of *N*-10(or 11)-chloroundecyl-ε-aminocaproic acid.

This acid solution was neutralized with sodium hydroxide pellets, and then 2.25 g. (0.057 mole) of sodium hydroxide was added in excess. The resulting solution was transferred to a 1-l. Erlenmeyer flask and an ethereal solution of 10.83 g. (0.057 mole) of *p*-toluenesulfonyl chloride was added. The mixture was then shaken mechanically for 6 hr., acidified with concentrated hydrochloric acid, and extracted several times with ether. The combined ethereal solution was evaporated to dryness and the resulting straw-colored, viscous liquid was dried for one day in a vacuum desiccator. A yield of 24.6 g. was obtained (91%); $n_D^{19.75}$ 1.5093. All attempts to induce crystallization of this compound were unsuccessful. An analysis of the crude compound gave the following results:

Anal. Calcd. for $C_{24}H_{40}NO_4SCl$: C, 60.79; H, 8.52; N, 2.96. Found: C, 62.56; H, 8.58; N, 3.14.

The infrared spectrum contains bands assignable to an aliphatic acid (1710, 2600–3200 cm.$^{-1}$), to a sulfonamide (1159, 1338 cm.$^{-1}$), and to a *para* substituted aromatic group (1604, 1503, and 813 cm.$^{-1}$).

In order to obtain a characterizable solid derivative of this compound, the *S*-benzyl thiuronium salt was prepared according to the direction of Donleavy.[5] The derivative was isolated in 93% yield having a crude melting point of 94.5–95.5°. After three recrystallizations from 80% ethanol, a product was obtained which melted at 97–97.5°.

Anal. Calcd. for $C_{32}H_{50}N_3O_4S_2Cl$: C, 60.02; H, 7.87; N, 6.56; Cl, 5.54. Found: C, 60.74; H, 8.04; N, 6.31; Cl, 4.73.

The infrared spectrum of a Nujol mull contains bands assignable to a carboxylic acid salt (1576, 1409 cm.$^{-1}$), to a sulfonamide (1340, 1160 cm.$^{-1}$), to *mono* and *para* substituted aromatic rings (1604, 1503, 695 and 813 cm.$^{-1}$), and to a thiuronium salt (1670, 2700–3100, 3200 and 3540 cm.$^{-1}$).

(3) The microanalyses were performed by Jozsef Nemeth, Lucy Chang, Maria Benassi, R. J. Nesset, and Ruby Ju, of the University of Illinois; Clark Microanalytical Laboratories, Urbana, Illinois; and Micro-Tech Laboratories, Skokie, Illinois. The infrared spectra were determined and interpreted by James Brader of the University of Illinois.

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N-p-Toluenesulfonyl-ϵ-aminocaproic acid. Sodium ϵ-aminocaproate was prepared according to the method of Galat.[6] Into a 500-ml. flask fitted with a reflux condenser were placed 67.8 g. (0.60 mole) of ϵ-caprolactam, 300 ml. of water, and 48.0 g. (1.2 moles) of sodium hydroxide. The solution was heated under reflux for 1 hr. and then cooled in an ice bath.

The sodium ϵ-aminocaproate was then converted into *N-p*-toluenesulfonyl-ϵ-aminocaproic acid by means of the general method of McChesney and Swann.[7] The alkaline solution of sodium ϵ-aminocaproate was transferred to a 1-l. Erlenmeyer flask and an ethereal solution, 114.4 g. (0.60 mole), of *p*-toluenesulfonyl chloride was added. After shaking the mixture mechanically for 6 hr., the ethereal layer was separated from the aqueous layer, and the aqueous solution was acidified to Congo red with dilute hydrochloric acid. The tosyl derivative, which crystallized immediately, was collected on a filter and dried overnight in a vacuum desiccator; yield 158 g. (92.4%). Recrystallization of the product from 25% ethanol yielded 141 g.; m.p. 106.5–108°; (reported 104–106°[8]).

Formation of N-p-toluenesulfonyl-ϵ-caprolactam in the attempted preparation of N-p-toluenesulfonyl-ϵ-aminocaproyl chloride. In a 100-ml. flask fitted with a reflux condenser were placed 28.5 g. (0.10 mole) of *N-p*-toluenesulfonyl-ϵ-aminocaproic acid and 41.65 g. (0.20 mole) of phosphorus pentachloride. The mixture was heated in an oil bath at 100° for 6 hr. After cooling, the reaction mixture was extracted with low petroleum ether. Evaporation of the petroleum ether, followed by distillation of the residual liquid under diminished pressure yielded a crude product which boiled from 150 to 180° at 5 mm. The distillation was accompanied by decomposition. The crude product solidified upon cooling and after two recrystallizations from cyclohexane an analytically pure sample was obtained which melted at 123–124.5°.

Anal. Calcd. for $C_{13}H_{17}NO_3S$: C, 58.40; H, 6.41; N, 5.24. Found: C, 58.32; H, 6.23; N, 5.35.

The infrared spectrum of a chloroform solution contains bands assignable to an imide (1696 cm.$^{-1}$), to a sulfonamide group (1358, 1172 and 676 cm.$^{-1}$), and to a para substituted aromatic ring (1604, 1502, and 813 cm.$^{-1}$).

Formation of N-p-toluenesulfonyl-ϵ-caprolactam in the attempted preparation of benzyl N-p-toluenesulfonyl-ϵ-aminocaproate. In a 500-ml. flask fitted with a Dean-Stark trap were placed 50.0 g. (0.175 mole) of *N-p*-toluenesulfonyl-ϵ-aminocaproic acid, 100 g. (0.93 mole) of benzyl alcohol, 200 ml. of dry benzene, and 1.0 g. of *p*-toluenesulfonic acid monohydrate. The solution was heated under reflux for one day, during which 1.9 ml. of water was expelled. After cooling to room temperature, the resulting solution was washed successively with six 50-ml. portions of 5% sodium bicarbonate solution, twice with 50 ml. of water, and once with 50 ml. of saturated sodium chloride solution. Solvent and benzyl alcohol were removed by distillation at reduced pressure and the residual liquid was fractionated through a 12-inch Vigreux column under diminished pressure. The distillation resulted in considerable decomposition; however, a crude product was isolated which boiled from 140–180° at 2.5 mm. Upon cooling, this material solidified. After two recrystallizations from 95% ethanol, an analytically pure sample was obtained which melted at 123–124.5°. The infrared spectrum of a chloroform solution is identical with that of the compound proved to be *N-p*-toluenesulfonyl-ϵ-caprolactam. A mixed melting point with the known compound showed no depression in melting point.

Benzyl N-benzoyl-ϵ-aminocaproate. *N*-Benzoyl-ϵ-aminocaproic acid was prepared from ϵ-caprolactam according to the method of Galat.[6]

In a 500-ml. flask fitted with a Dean-Stark trap were placed 50.0 g. (0.21 mole) of *N*-benzoyl-ϵ-aminocaproic acid, 100 g. (0.93 mole) of benzyl alcohol, 200 g. of dry benzene, and 2 ml. of concentrated sulfuric acid. The solution was heated under reflux for 12 hr. and then allowed to cool to room temperature. The solution was then washed successively with three 50-ml. portions of 5% sodium bicarbonate solution, four 50-ml. portions of water, and once with 50 ml. of saturated sodium chloride solution. Solvent and excess benzyl alcohol were removed by distillation at reduced pressure, using the water aspirator. Final distillation of the residual liquid under diminished pressure yielded 63.0 g. (91%); b.p. 250–255° (0.3 mm.); m.p. 62–65°; $n_D^{21.25}$ 1.5568. After four recrystallizations from 80-20 cyclohexane-benzene solution, an analytically pure sample was obtained; m.p. 64.5–66°.

Anal. Calcd. for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 74.06; H, 7.08; N, 4.35.

The infrared spectrum of a chloroform solution contains bands assignable to an amide (1660, 3455 cm.$^{-1}$), and to an aliphatic ester (1728, 1220–40 cm.$^{-1}$).

Benzyl N-formyl-ϵ-aminocaproate. ϵ-Aminocaproic acid was prepared from ϵ-caprolactam according to the method of Meyers and Miller.[9] The amino acid was then converted to the *N*-formyl derivative by the procedure of Coffman, Cox, Martin, Mochel, and Van Natta.[10]

In a 500-ml. flask fitted with a Dean-Stark trap were placed 25.0 g. (0.157 mole) of *N*-formyl-ϵ-aminocaproic acid, 50.0 g. (0.46 mole) of benzyl alcohol, 200 ml. of dry benzene, and 1.5 ml. of concentrated sulfuric acid. The reaction mixture was heated under reflux for one day during which 2.7 ml. of water was expelled. After cooling to room temperature, the resulting solution was washed successively with five 50-ml. portions of 5% sodium bicarbonate solution, three 50-ml. portions of water, and finally once with saturated sodium chloride solution. Solvent and excess benzyl alcohol were removed by distillation at reduced pressure. The remaining liquid was distilled under diminished pressure yielding 8.85 g. (23%); b.p. 235° (8 mm.); $n_D^{22.5}$ 1.5210. (Extensive decomposition occurred during the distillation making it almost impossible to maintain a constant pressure.)

Anal. Calcd. for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 68.28; H, 7.95; N, 5.41.

The infrared spectrum contains bands assignable to a formamide (1670, 3270 cm.$^{-1}$) and an aliphatic ester (1735, 1163 cm.$^{-1}$).

In an effort to obtain an analytically pure product, the above crude sample was refractionated through a 10-inch Vigreux column under diminished pressure. Complete decomposition of the ester occurred. Benzyl alcohol and ϵ-caprolactam were shown to be the products of the decomposition.

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